(51) International Patent Classification 6 :		(11) International Publication Number:	**WO 00/24676**
C01F 17/00, 7/02, C01G 37/02, 25/02, 23/047, C22B 11/00	A1	(43) International Publication Date:	4 May 2000 (04.05.00)

(71) Applicant (for all designated States except US): UNIVERSITY OF UTAH [US/US]; Technology Transfer Office, Suite #110, 615 Arapeen Drive, Salt Lake City, UT 84108 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): VIRKAR, Anil, Vasudeo [US/US]; University of Utah, Materials Science & Engineering, Room 304, 122 S. Central Campus Drive, Salt Lake City, UT 84112-0560 (US). BHIDE, Sanjeevani, Vidyadhar [IN/US]; Apt. N304, 3400 Kent Avenue, Metairie, LA 70006 (US).

(74) Agent: SONNTAG, James, L.; P.O. Box 21, Heber City, UT 84032 (US).

(54) Title: A MOLECULAR DECOMPOSITION PROCESS FOR THE SYNTHESIS OF NANOSIZE CERAMIC AND METALLIC POWDERS

(57) Abstract

A process is disclosed for forming a nanosize ceramic powder. A precursor ceramic material is formed of a fugitive constituent and a non-soluble constituent in a single phase. The precursor is contacted with a selective solvent (water, acid, etc.) to form a solution of the fugitive constituent in the solvent and a residue of the non-soluble constituent. The precursor is sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and form the nondissolved residue of the non-soluble constituent. The precursor material and the non-soluble residue are sufficiently insoluble in the solvent such that there is insufficient precursor material and non-soluble residue in solution to deposit and precipitate upon the residue of the non-soluble-constituent. The fugitive constituent is sufficiently soluble in the solvent such that the precursor reacts with the solvent to form the solution of the fugitive constituent without precipitation and deposition of fugitive constituent upon the residue of the non-soluble constituent in the form of nanosize particles. After the fugitive constituent is dissolved the selective solvent containing the fugitive constituent is removed from the residue. The residue remains in the form of a nanosize powder of the non-soluble constituent.

TITLE

A MOLECULAR DECOMPOSITION PROCESS FOR THE
SYNTHESIS OF NANOSIZE CERAMIC AND METALLIC
POWDERS

5   STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

10   FIELD OF THE INVENTION

This invention relates to a process for forming ceramic powders with fine
nanosize particles.

BACKGROUND OF THE INVENTION

Nanosize powders are generally considered to be powders having very fine
15   particles in the nanometer range, i.e., less than a few nanometers, e.g., 100 nanometers
or less, usually 10 nanometers or less.

Nanosize powders have numerous applications such as catalysts,
electrocatalysts, catalyst supports, electrodes, active powders for the fabrication of
dense bodies, semiconductors for energy storage, photovoltaics, ultrafine magnetic
20   materials for information storage, environmental clean-up as destructive adsorbents,
water purification, information storage, and optical computers, to name a few. Some
of the numerous examples include the following: nanosize (3 to 4 nm) platinum for
oxygen reduction in acid electrolytes, many metallic powders made by precipitation in
aqueous and non-aqueous media for alloy fabrication and for catalysis, nanosize iron
25   oxide catalyst for coal liquefaction, nanosize iron oxide particles for magnetic
applications, tetragonal zirconia powder by a hydrothermal treatment at high pressures
for structural applications, carbides and nitrides using non-aqueous media, nanosize
$BaTiO_3$ by a gas-condensation process, etc. Many oxides have potential applications

as nanosize powders. These include: $CeO_{(2-x)}$ for catalytic reduction of SO_2, γ-alumina as a catalyst support and for enhancing ionic conductivity of lithium iodide, V_2O_5 as a catalyst for NO_x reduction, and etc. Several processes currently used for the synthesis of nanosize powders include:(1) Gas-phase condensation, (2) Mechanical milling, (3) Thermal crystallization, (4) Chemical precipitation, (5) Sol-gel processing, (6) Aerosol spray pyrolysis, and etc.

In gas-phase condensation, evaporation of precursors and their interaction with an inert gas leads to loss of kinetic energy, and homogeneous nucleation of nanosize powders occurs in a supersaturated vapor. Nanocrystalline powders of TiO_2, Li_2O-doped MgO, CeO_2, Y-doped ZrO_2, etc. have been produced by gas-phase condensation. Aerosol spray pyrolysis has been used to synthesize $BaFe_{12}O_{19}$, Fe_2O_3 among some other materials. High-energy mechanical milling is used extensively to produce nanostructured materials, especially when large quantities of materials are required. Very fine particles of nickel-aluminum alloy, Fe-Co-Ni-Si alloys, Ni-Mo alloys, for example, have been produced by mechanical milling. Contamination by the milling process, however, is a shortcoming of this process. Also, although very fine (nm size) particles can be made, agglomeration is a problem leading to cluster sizes in the micron range.

Chemical coprecipitation has received considerable attention for the synthesis of nanosize powders. Metallic as well as ceramic powders can be made by a careful control of chemistry. Alkali metal borohydride, MBH_4 where M is an alkali metal, for example, has been used as a reducing agent in aqueous media for the synthesis of metallic powders. Similarly, hydroorganoborates of the general formula $MH_v(BR_3)$ or $MH_v[BR_n(OR')_{3-n}]_v$ where M is an alkali or alkaline earth metal, $v = 1, 2$, and R, R' are alkyl or aryl groups have been used as reducing and precipitating agents. It is important to control pH and ionic strength in aqueous media to prevent Ostwald ripening. In the synthesis of nanosize iron oxide, for example, it has been shown that the higher the pH and the higher the ionic strength, the smaller is the size of nanosize Fe_3O_4 particles.

In most methods for the synthesis of nanosize powders, two issues are particularly important; (1) the formation of fine, uniform size particles, and (2) the prevention of agglomeration. Nanoparticles of a uniform size can in principle be formed by carefully controlling nucleation and growth. Often, a variety of

5 encapsulating methods are necessary to control the size of nanoparticles.

Agglomeration is often the result of Van der Waal's forces. The adverse effect of agglomeration on the sintering behavior of ceramic powders is well documented. Even in catalysis, the need for dispersed powders is well known. Often, supercritical drying can be used to obtain nonagglomerated powders. In liquid media,

10 agglomeration can be suppressed through steric hindrance or through the manipulation of electrostatic interactions. The latter in polar liquids can be achieved by changing the pH and the ionic strength of the solution. Many techniques involve the use of surfactants. Often the powders which are nonagglomerated and well dispersed in a liquid, tend to agglomerate during the drying stage. Fortunately, methods such as

15 slip-casting, gel-casting, pressure slip casting can be used to achieve powder compaction in a wet state. Such has been demonstrated using submicron ceramic powders.

With the exception of milling, all the above methods are based on molecular synthesis of nanoparticles wherein the particles are built-up by atom-by-atom, or

20 molecule-by-molecule, addition. Even in processes based on the decomposition of metal carbonyls, the growth of particles occurs by a layer-by-layer addition of atoms. As a result, a control of nucleation and growth is necessary to ensure the formation of nanosize particles. This often requires a very precise and difficult control of the reaction system, which renders the manufacture of the nanosize powder in large

25 quantities impractical or impossible. In addition, the molecular synthesis processes are costly because of the relatively large capital expenditures required for the equipment to control the formation of only a small quantity of nanosize product..

Objects of the Invention

It is, therefore, an object of the invention to provide method for the formation of nanosize powders that is easy to implement on an industrial scale and in relatively inexpensive when compared to molecular synthesis methods.

Another object of the invention is to provide a method in which nanosize powders are formed by a process other than precipitation or deposition from solutions, thus eliminating the possibility of unwanted deposition and growth of the nanosize powders.

Another object of the invention is to provide a method which forms nanosize powders that have a reduced tendency to agglomerate.

Another object of the invention is to provide a method for the formation of nanosize powders that can be applied to forming a variety of powder compositions.

Further objects of the invention will become evident in the description below.

BRIEF SUMMARY OF THE INVENTION

In order to overcome the problems associated with molecular synthesis and milling to form nanosize powders, the present invention presents an alternative approach for the synthesis of nanosize powders. In the present invention, a precursor inorganic compound is formed from which the unwanted component is leached away so that a fine, nanosize powder is left as a residue. Thus, the present invention is based on molecular decomposition, rather than molecular synthesis, or deposition.

As discussed above, one of the problems with many methods of synthesis of nanosize powders is that often it is difficult to synthesize large quantities of materials. By contrast, the present invention is suitable for making large quantities of nanosize powders of a number of materials.

In summary, the present invention is a process for forming nanosize powders . The process comprises:

forming a precursor ceramic material comprising a fugitive constituent and a non-soluble constituent in a single phase;

contacting the precursor material a selective solvent to form a solution of the fugitive constituent and a residue of the non-soluble constituent,

the precursor sufficiently reactive with the solvent to form the solution of the fugitive

constituent in the solvent and the residue of the non-soluble constituent

the precursor material and the non-soluble residue sufficiently insoluble in the solvent

such that there is insufficient precursor material and non-soluble residue in solution to

5   deposit and precipitate upon the residue of the non-soluble-constituent,

the fugitive constituent being sufficiently soluble in the solvent such that the precursor

reacts with the solvent to form a solution of the fugitive constituent without

precipitation and deposition of fugitive constituent upon the residue of the non-soluble

constituent in the form of nanosize particles;

10   removing the selective solvent solution from the residue to form a nanosize

powder having the same chemical composition as the non-soluble constituent.

        The precursor material should be insoluble as the precursor material in the

solvent. One of the objects of the present invention is to prevent deposition or

precipitation of dissolved materials upon the nanosize particles that are formed from

15   the non-soluble residue freed of the fugitive constituent. Deposition or dissolved

precursor material will not only contaminate the residue, but possibly result in

particles that are too large. In the present invention, an object is to prevent, as much

as possible, deposition of dissolved materials and the resulting growth of existing

crystals. Unlike prior-art methods where small crystals are crystallized from solution,

20   it is practical in the present invention to inhibit the crystallization and precipitation

process altogether, as crystallization is not required to form initial nanosize crystals.

Accordingly, as further illustrated below, a precursor is chosen such that precipitation

of any material upon the nanosize particles is essentially avoided.

        Another requirement of the precursor material is that it be reactive with the

25   solvent. Since the precursor is insoluble, the precursor composition does not dissolve,

but it does react to selectively remove the fugitive constituent, leaving a freed non-

soluble constituent.. The fugitive constituent is sufficiently soluble that it will not

precipitate from the solution to contaminate and grow the particles of the non-soluble

constitituent. The non-soluble constituent is essentially insoluble to prevent dissolved

30   material dissolving into the solution, there thereafter precipitating upon and growing

the nanosize particles of the non-soluble material formed by removal of the fugitive

constituent. Basically, the invention involves a balance between preventing precursor and non-soluble constituent from forming a solution so that it cannot redeposit and grow crystals, and removing the fugitive constituent, that is sufficiently soluble in the solution that it will not precipitate from the solution to grow crystals.

5   For example, $BaCeO_3$ does not dissolve in water, but reacts with water to form a solution of the Ba (as $Ba(OH)_2$). On the contrary, $NaAlO_2$ is soluble in water, and cannot be used as a suitable precursor for the present invention.

In order that the non-soluble constituent freed from the fugitive constituent form nanosize particles, the precursor should be a single phase material, i.e., where
10   the differentiation between the non-soluble and the fugitive constituents is on a molecular level. Accordingly, the precursor exists as a compound existing is the form of a large molecule, or as an alloy. For ceramics, an example of a precursor material is a mixed oxide with at least two cations, the metal oxide of the first cation being soluble to function as the fugitive constituent, and the oxide of the second being non-
15   soluble to function as the non-soluble constituent. For forming metal nanosize powders, the precursor can exist, for example, as an alloy or an intermetallic compound.

The solvent is selected to react with the precursor and have the solubility properties as described above. For ceramics, a preferred solvent is water, but non-
20   aqueous solvents may be required to suppress the solubilities of the non-soluble residue and/or the precursor. Usually the solvent is polar, as the fugitive constituent, which must be solubilized, is often a polar composition. Typically, suitable solvents for forming a ceramic nanosize powder are polar liquids that solubilize selected ceramic oxides, which selected oxides in the process of the invention are the fugitive
25   constituents. As further described below, preferred solvents are water and acids. For metallic nanosize powders, the selective solvent is typically an acid that reacts with or dissolves the fugitive metal, and not the non-soluble metal.. In place of acids, an acid gas such as SO_3, N_2O_5, CO_2 or HCl, may be used to react with and remove the fugitive constituent.

30   Any suitable process may be used for forming a precursor is contemplated. For example, where the precursor is a mixed ceramic subjecting a powder mixture to a

suitable high-temperature treatment is suitable. Precursors for metallic powders are likewise formed by any suitable process to produce a suitable alloy or intermetallic compound, such as alloying methods or powder metallurgy.

The solvent is then removed from the remaining non-soluble constituent.

5 With the fugitive constituent removed, the non-soluble constituent assumes the form of nanosize particles. The solvent is removed by conventional methods, including, but not limited to settling, centrifugation, filtering, air drying, or a combination or the above. The solvent, may also be removed by replacing it with another liquid, such as replacing at aqueous solvent with an alcohol, and then separating the powder from the

10 replacement liquid. Using a replacement liquid may be desirable to inhibit agglomeration of the powder during drying.

The product is chemically the same as the non-soluble constituent. The process of the invention is particularly suitable for synthesizing nanosize powders of Al_2O_3, CeO_2, ZrO_2, TiO_2, V_2O_5, rare earth (RE) oxide-doped CeO_2 and RE- or

15 Y_2O_3-doped ZrO_2.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic showing a reaction illustrative of the process of the invention

Figure 2(a) is an XRD (X-ray diffraction) trace of a single-phase perovskite

20 precursor material (Gd-doped $BaCeO_3$).

Figure 2(b) is an XRD trace of the material of Figure 2(a) after boiling in water for two days, showing conversion to nanosize CeO_2.

Figure 2(c) is an XRD trace of a comparative coarse (not nanosize) CeO_2 powder.

25 Figure 3(a) is an XRD trace of an as-received, precursor (non-nanosize) Na_2ZrO_3 powder.

Figure 3(b) is an XRD trace of the residue after boiling the Na_2ZrO_3 of Figure 3(a) in water for 10 minutes.

Figure 3(c) is an XRD trace of the residue from the boiling of Na_2ZrO_3 from

30 Figure 3(c) after heating in air to 100°C for 1.5 hours.

Figure 3(d) is an XRD trace of the residue after 1.5 hours in air at 200°C.

Figure 3(e) is an XRD trace of the residue after 1.5 hours in air at 300°C.

Figure 3(f) is an XRD trace of the residue after 1.5 hours in air at 350°C.

Figure 3(g) is an XRD trace of the residue after 1.5 hours in air at 400°C.

Figure 3(h) is an XRD trace of the residue after 1.5 hours in air at 500°C.

Figure 3(i) is an XRD trace of the residue after 1.5 hours in air at 600°C.

DETAILED DESCRIPTION OF THE INVENTION

Synthesis of Precursor Powders:

The present invention is suitable for the synthesis of many types of powders. Although the following discussion is confined to specific materials, the applicability of the present invention to other powders will be evident to one of ordinary skill in the art. For the purposes of discussion, rare earth (RE)-doped CeO_2 and Y_2O_3-doped ZrO_2 are used as examples. Y_2O_3-doped ZrO_2 has many applications such as in oxygen sensors, solid oxide fuel cells, as a constituent in electrodes and in structural ceramics. RE-doped CeO_2 has applications in oxygen separation membranes, in fuel cells as well as in catalysis.

Respective precursor powders can be synthesized using conventional processing methods. For example, for the synthesis of nanosize RE_2O_3-doped CeO_2 by the present invention, a precursor can be $BaCe_{(1-x)}RE_xO_{(3-\delta)}$. The precursor is synthesized using $BaCO_3$, RE_2O_3 and CeO_2 in a powder form, mixing reagent powders, and calcining at 1250°C. A similar procedure can be used for other materials such as Y_2O_3-doped ZrO_2. Other examples included $BaCe_{(1-x)}RE_xO_{3-\delta}$ or $SrCe_{1-x}RE_xO_{3-\delta}$ precursors for a composition of the final nanosize powder is $Ce_{1-x}RE_xO_{2-\delta}$, or $BaZr_{1-x}RE_xO_{3-\delta}$ or $BaZr_{1-x}REXO_{3-\delta}$ precursors for a composition of the nanosize powder of $Zr_{1-x}RE_xO_{2-\delta}$ RE is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and about 0.13.

Synthesis of Nanosize Powders from the Precursor:

Synthesis of the nanosize powders from the precursor involves exposing the precursor to a selective solvent that leaves the desired component. The following approaches can be used be used:

5   (a) A reaction with water.

(b) A reaction with a dilute acid such as HNO_3, HCl, H_2CO_3, and H_2SO_4.

(c) A reaction with CO_2 and SO_3 in polar, non-aqueous solvents.

(a) A Reaction with Water:

Water is the ideal solvent. Also, in many cases, thermodynamics of the

10   formation of alkali hydroxides or alkaline earth hydroxides are favorable. There are, however, a few potential complications, in particular many elements form hydroxides, and there is the danger of agglomeration during the drying stage. For example, in the synthesis of ZrO_2 the undesired formation of $Zr(OH)_4$ is possible. However, it has been shown that with Na_2ZrO_3 as a precursor, a direct reaction with water can be

15   readily effected without the formation of $Zr(OH)_4$. The potential for agglomeration can be suppressed by replacing the water with alcohol after solvation.

(b) A Reaction with Acids:

In many cases, reaction with water is not favorable. For example, reaction of $BaZrO_3$ with water to form ZrO_2 and $Ba(OH)_2$ is not favored. However, as shown in

20   Table B, reaction of $BaZrO_3$ with HNO_3 or N_2O_5 to form $Ba(NO_3)_2$ and ZrO_2 is favored. Also, $Ba(NO_3)_2$ has a reasonable solubility in water. With HNO_3 as a reactant, the formation of $Zr(OH)_4$ is suppressed. The tendency for agglomeration can be minimized, by either replacing water with an alcohol or other organic liquids of high vapor pressures, or drying under supercritical conditions. It is also within

25   contemplation of the invention to use surfactants to minimize agglomeration, either based on electrostatic interactions or steric effects.

(c) Reactions with non-aqueous electrolytes - Reactive gases in Polar, Non-aqueous Solvents:

This approach is particularly suitable when there is a tendency to form hydroxides of the product oxides which precludes the use of water when the objective
5   is to synthesize nanosize powders with minimal agglomeration. In such cases, the use of non-aqueous, polar liquids may be necessary. Table C lists a few non-aqueous solvents, which are used for non-aqueous electrolytes. The polar liquid used as a solvent should also have a reasonable solubility for the reacting gas, which may be, for example, CO_2, SO_3, SO_2, or N_2O_5.

10   Suitable solvents are selected based on the following criteria: (i) the solubility of the reacting gas in the solvent, and (ii) the solubility of the fugitive compound formed; e.g. $BaCO_3$ or $BaSO_4$ in the case of CO_2 or SO_3. In order to increase contact between the precursor powder (e.g. $BaGd_xCe_{(1-x)}O_{(3-\delta)}$ x=0-.25, δ=0-0.13) and the gas (CO_2 or SO_3), the suspension of the powder is preferably agitated, e.g. by
15   constant stirring, while the gas is bubbled through it. The solvent vapors are also preferably recovered and returned back to the reactor, by using, for example, a water-cooled condenser.

Mechanism of the Kinetics of Synthesis of Nanosize Powders:

The kinetics of the formation of nanosize powders is a factor that should be
20   considered in choosing the precursor and solvent for the desired. The data in Table B give the thermodynamic basis for the occurrence of certain given reactions. Assuming a given reaction is favored over undesired competing reactions, an important consideration is the kinetics of the reaction. With reference to the schematic of the reaction given in Figure 1, it is readily seen that the kinetics of the reaction should
25   depend upon the transport of soluble reactants and products. The overall reaction mechanism is expected to involve the following steps; (a) The transport of the dissolved reacting gas, e.g., N_2O_5, CO_2 or SO_3, (or the respective acids) through the porous layer formed to the interface separating the precursor and the product, (b) Reaction at the interface, and (c) The transport of the dissolved byproduct, e.g.,
30     $Ba(NO_3)_2$, $BaCO_3$ or $BaSO_4$, from the interface through the porous layer, into the

- 10 -

bath. The overall kinetics may be influenced by all three of the factors, and may be dictated by whichever is the slowest step. The solubility of the reacting gas is a function of pressure; the higher the pressure, the higher is the solubility. Both the kinetics of the actual reaction occurring at the interface as well as the transport through the porous layer are functions of the concentration of the dissolved reactant species; the higher the concentration, the faster should be the kinetics. The temperature dependence of the reaction at the interface, however, will in general be different from that of the transport of dissolved species. The known theoretical models of transport through porous bodies can be used in this analysis.

Propensity for Particle Growth:

The advantage of the present invention over the other methods for the synthesis of nanosize powders is that there is negligible tendency for the occurrence of particle growth by either Ostwald ripening or by precipitation. This is because neither the precursor nor the desired product, are soluble in the solvent. For example, neither $BaCeO_3$ nor CeO_2 is soluble in water; only the leachable $Ba(OH)_2$ is soluble in water. Since the product is nanosize, it could be argued that its solubility may be higher than bulk materials. It is known, for example, that the solubility of a sparingly soluble species is related to its size by the following equation;

$$C(r) \approx C(\infty)\exp\left[\frac{2\gamma\Omega}{rk_BT}\right]$$

where, $C(\infty)$ is the bulk solubility (particle of a large radius), $C(r)$ is the solubility of a particle of radius r, γ is the particle-solvent interfacial energy, Ω is the molecular volume of the particle, k_B is the Boltzmann constant, and T is the absolute temperature. Assuming the following values for the various parameters; particle radius, r ~2 nm, interfacial energy, γ ~0.5 J/m², molecular volume, Ω ~0.125 nm³ (125 Å³), and the temperature, $T = 350°K$, then the ratio $C(r)/C(\infty)$ is about 3.6. This shows that as long as $C(\infty)$ is rather low, even for nanosize particles the solubility enhancement is not large enough to cause any Ostwald ripening. Thus, there should be negligible particle growth.

Sintering Behavior of Powders:

The sintering (densification) behavior of nanosize powders synthesized by the present invention is expected to result in densification at lower temperatures, resulting in a finer microstructure.

5   *Characterization of Sintered Bodies:*

The grain size of sintered bodies made from the nanosize powders should be smaller than those made from conventional ceramic powders. It is well known that very fine-grained ceramics often exhibit interesting properties, such as, for example, superplasticity at elevated temperatures, and high strength at low temperatures.

10   *Metallic Powders:*

The present invention is also applicable to the synthesis of metallic powders, by the appropriate choice of the metallic precursor and the selective solvent. For example, synthesis of Pd powder can be achieved with precursor of an equimolar alloy of Ba and Pd, which is actually a line compound BaPd. The alloy can be made by arc melting or by powder metallurgy. The powdered alloy is then treated in dilute

15   HCl to remove the Ba to form nanosize Pd.

Suitability for the Synthesis of Large Quantities of Nanosize Powders:

The process of the invention for the synthesis of nanosize powders is simple, and can be adapted by using chemical leaching technology. Especially with water as the solvent, the process does not require exotic equipment nor exotic precursors. The

20   precursors can be made by simple calcination or alloy fabrication methods. The starting particle size of the precursors need not be very small. Finally, the process has a general applicability for a wide range of materials. The process thus is easily amenable to scale up for production of large quantities of materials.

25   In summary, nanosize powders of a variety of materials are usually made by one or more processes which may be categorized as belonging to <u>molecular synthesis</u> wherein particles are built up by an atom-by-atom or a molecule-by-molecule addition on a particle nucleus. The present invention is based on <u>molecular decomposition</u> wherein unwanted species are chemically leached away thus producing a nanosize

- 12 -

powder as a residue, starting with a precursor of a macroscopic size. The method of the present invention should result in nanosize particles of a uniform composition and size. In the present invention, neither the precursor nor the product is soluble in the reaction medium. As a result, particle coarsening is not expected to occur.

5   EXAMPLES

The following describes a general approach of the practice of the invention with two illustrative examples; namely the synthesis of nanosize CeO_2 and ZrO_2.

Example I

Synthesis of Nanosize CeO_2:

10   The starting precursor may be one of the alkaline earth cerates, such as $BaCeO_3$. At room temperature, the standard free energy for the reaction

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2$$

is - 189.79 kJ/mol. indicating that this reaction is favored. The volume of CeO_2 per molecule is ~77 $Å^3$ and the linear dimension is (cube root of the volume) 4.25 Å. The

15   volume per molecule of $BaCeO_3$ is ~85 $Å^3$ and the linear dimension is 4.4 Å. Thus, if BaO is leached out as $Ba(OH)_2$, the change in volume for the original $BaCeO_3$ is ((85 - 77)/85) x 100 or 9.4%, or the change in linear dimension is ((4.4 - 4.25)/4.4) x 100 or 3.4%. Figure 1 shows a schematic of a particle 11 reacting with H_2O to form $Ba(OH)_2$. The $Ba(OH)_2$ formed dissolves into water thus leaving a porous layer 13 of

20   CeO_2. The volume percent porosity in the layer is expected to be about 9.4%. The fact that $BaCeO_3$ readily reacts with water suggests that the porosity is open. This facilitates the transport of the reacting species, H_2O here, to the CeO_2 (porous)/$BaCeO_3$ (dense) interface 15. The reaction continues until all of the $BaCeO_3$ 17 reacts to form porous CeO_2. The formed CeO_2 should be fragile and

25   break into a fine, nanosize powder.

In order to verify the concept, the following preliminary experiments were done. Gd_2O_3-doped $BaCeO_3$ powder of composition $BaGd_{0.2}Ce_{0.8}O_{(3-\delta)}$ was synthesized using $BaCO_3$, CeO_2, and Gd_2O_3 powders. The powders were mixed in

- 13 -

requisite proportions and wet ball-milled for 24 hrs. The well-mixed powder was then

dried and calcined at 1450°C for 6 hrs. The calcined powder was then ball-milled and

examined by X-ray diffraction (XRD) with CuK_α radiation to ensure the existence of

a single-phase perovskite (Figure 2(a)). The calcined powder was then boiled in water

5   for 2 days, filtered using a fine filter paper, washed with water to dissolve away

$Ba(OH)_2$, dried and then examined by XRD. Figure 2(b) shows the corresponding

XRD trace. Also shown in Figure 2(c) is an XRD trace of as-received CeO_2. A

comparison of Figures 2(a) and 2(b) shows that upon boiling, $BaCeO_3$ completely

decomposes. The sharp peak at ~24° is due to remnant $Ba(OH)_2$ not removed

10   completely during washing.

A comparison of Figures 2(b) and 2(c) shows that the powder formed upon

boiling is indeed CeO_2 (presumably Gd-doped). The important difference between

the two is that the XRD peaks of the powder formed by boiling $BaCeO_3$ are

considerably broader than for the as-received CeO_2 powder. Using the Scherrer

15   formula, the particle size of the ceria formed is estimated to be ~4 nm. This shows

that the method of the present invention involving molecular decomposition of

starting a starting material with a larger molecule can lead to a fine, nanosize powder

even when the initial powder is quite coarse.

Example II

20   *Synthesis of Nanosize ZrO_2:*

The starting precursor may be a suitable alkali or alkaline earth zirconate. In

the preliminary work, Na_2ZrO_3 was used as the precursor. This was simply boiled in

water for a few minutes. The reaction is

$$Na_2ZrO_3 + H_2O \rightarrow ZrO_2 + 2NaOH$$
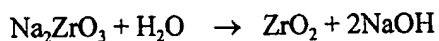
25   No thermodynamic data are available. However, preliminary experimental work,

results of which are described below, shows that the above reaction is indeed favored..

Powder of Na_2ZrO_3 was purchased from a commercial vendor. Approximately

10 gms. of the powder was boiled in water for ten minutes. The residue was filtered,

washed, and dried. The residue was subsequently examined by X-ray diffraction

(XRD) with CuKα radiation. The residue was then subjected to a number of thermal treatments. The following are the results of this experiment.

Figure 3(a) is an XRD trace of the as-received Na_2ZrO_3 powder. Sharp peaks indicate a relatively coarse (at least a few tenths of a micron or more) particle size. Very tiny peaks at approximately 28 and 31.5 degrees are due to a small amount of monoclinic ZrO_2 that was present in the as-received Na_2ZrO_3 powder.

Figure 3(b) is an XRD trace of the residue after boiling Na_2ZrO_3 in water for 10 minutes, washing and drying. The trace shows the absence of the original Na_2ZrO_3 powder. The trace mainly consists of two very broad peaks. These peaks belong to the cubic phase of ZrO_2. The peaks are very broad and contain more than one peak in each of the peaks. These very broad peaks are indicative of a very fine (nano) particle size. The reaction that occurred is the following:

$$Na_2ZrO_3 + H_2O \rightarrow ZrO_2 + NaOH$$
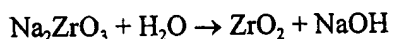
The two sharp peaks at ~28 and ~31.5 degrees are again due to the small amount of monoclinic ZrO_2, present in the original Na_2ZrO_3 powder.

Note that the intensity scales in 3(a) and 3(b) are quite different, and that the same monoclinic peaks with about the same intensities are present in Na_2ZrO_3. Note also that the integrated peak intensity of the monoclinic peak is very small compared to that of the nanosize ZrO_2 formed (broad peaks). Some growth of the original monoclinic ZrO_2 particles is expected by the deposition of new ZrO_2 (by the above reaction) on them. These monoclinic ZrO_2 particles are not expected to be nanosize, consistent with observations.

Figure 3(c) is an XRD trace of the residue after heating in air to 100°C for 1.5 hours. Note that the trace is similar to that in Figure 3(b).

Figure 3(d) is an XRD trace of the residue after 1.5 hours in air at 200°C in air. The peaks have become somewhat sharper (peak widths are less in this figure as compared to that in Figures 3(b) and 3(c)). This is indicative of a slight coarsening of particles.

Figure 3(e) is an XRD trace of the residue after 1.5 hours in air at 300°C. The peaks not only have become sharper but that the initial very broad peaks of the residue have now split into more peaks. A total of 4 broad peaks are apparent, in addition to

- 15 -

the two sharp peaks corresponding to the original monoclinic ZrO_2. The four broad peaks are identified with cubic ZrO_2. The peaks correspond to (111), (200), (220), and (311) reflections, in increasing diffraction angle.

Figure 3(f) is an XRD trace of the residue after 1.5 hours in air at 350°C. The four peaks have become slightly sharper.

Figure 3(g) is an XRD trace of the residue after 1.5 hours in air at 400°C. The four peaks have become even sharper.

Figure 3(h) is an XRD trace of the residue after 1.5 hours in air at 500°C.

Figure 3(i) is an XRD trace of the residue after 1.5 hours in air at 600°C.

The corresponding XRD traces in Figures 3(c) to 3(i) show the formation of cubic zirconia as the residue is heated to higher temperatures.. The stable phase of ZrO_2 at low temperatures is monoclinic. The formation of a very fine (nanosize) ZrO_2 by the described process leads to the stabilization of cubic ZrO_2 due to surface energy considerations ($\gamma_{Cubic} < \gamma_{Monoclinic}$ where γ denotes surface energy of the respective polymorph). The present experiment showed that: (1) Na_2ZrO_3 can be used to synthesize nanosize ZrO_2. (2) The nanosize ZrO_2 formed is of cubic crystal structure. Using the Scherrer formula, which relates the particle size, d, to peak broadening, B, diffraction angle, θ, and X-ray wavelength, λ, by

$$d = \frac{0.9\lambda}{B\cos\theta}$$

the particle size of the ZrO_2 formed as a function of subsequent heat treatment temperature was calculated. The calculated particle size as a function of thermal treatment is given in Table A.

Table A

Nanosize ZrO_2 powders produced by reaction of Na_2ZrO_3 with water.

Temperature (°C)	Corrected (111) Peak Width (rad)	Particle Size (nm)
300	0.0476	3.4
350	0.0371	4.3
400	0.0164	9.8
500	0.0124	13.0
600	0.0113	14.2

The preceding two examples demonstrate the approach and the potential of the present invention for the synthesis of nanosize oxide powders.

The preceding shows that nanosize CeO_2 and ZrO_2 can be produced respectively by leaching out BaO from $BaCeO_3$, as $Ba(OH)_2$ and Na_2O from Na_2ZrO_3, as $NaOH$. Various other reacting species can also in principle be used. As an example, let us examine the formation of Al_2O_3 starting with $BaAl_2O_4$ by reacting it with HNO_3 by the following reaction.

$$BaAl_2O_4 + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O + Al_2O_3$$

The free energy for the above reaction at room temperature is - 255.35 kJ/mol.. The change in volume upon removing BaO is ~59% and the change in linear dimension is ~17%. Note that volume percent porosity in this case is much higher than for $BaCeO_3 \rightarrow CeO_2$ conversion and the reaction is expected to progress with ease. In general, the greater the amount of material that has to be leached away per unit amount of the desired final product, the finer should be the particle size. In this context, with $Ba_3Al_2O_6$ as a precursor is superior since three molecules of BaO have to be removed to form one molecule of Al_2O_3. The standard free energy for the reaction.

$$Ba_3Al_2O_6 + 6HNO_3 \rightarrow 3Ba(NO_3)_2 + Al_2O_3 + 3H_2O$$
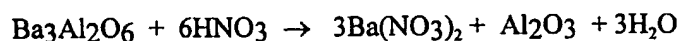
at room temperature is −884.15 kJ/mol. indicating that the reaction is favored. The percent change in volume per one molecule of Al_2O_3 formed is greater than with $BaAl_2O_4$, implying a greater porosity, potentially faster kinetics, and a potentially finer particle size. A similar reaction can be envisioned with H_2CO_3 as the reactant. However, $BaCO_3$ has negligible solubility in water. With HNO_3 as the reactant, several reactions are possible. One such successfully conducted in our laboratory is the reaction of $MgTiO_3$ with HNO_3 to form $Mg(NO_3)_2$ and TiO_2 given by

$$MgTiO_3 + 2HNO_3 \rightarrow Mg(NO_3)_2 + TiO_2 + H_2O$$

The above reaction is thermodynamically favored at room temperature. Also, $Mg(NO_3)_2$ is water soluble. Preliminary experiments were done wherein $MgTiO_3$ was boiled in dilute HNO_3 for 11 hours. The reaction went to completion and the

resulting TiO_2 was indeed nanosize, as judged by XRD peak broadening. The XRD traces are not given here for the sake of brevity.

The preceding discussion was on reactions of precursor powders with HNO_3. It is also possible and advantageous to use H_2SO_4 since the magnitudes of standard

5   free energies ($|\Delta G^\circ|$ with $\Delta G^\circ < 0$) of the corresponding reactions are often larger with H_2SO_4 than with HNO_3. As an example of the use of SO_3, consider the synthesis of V_2O_5, which is used as a catalyst in NO_x reduction, starting with $Na_4V_2O_7$. Reaction with SO_3 is given by

$$Na_4V_2O_7 + 2H_2SO_4 \rightarrow 2Na_2SO_4 + V_2O_5 + 2H_2O$$
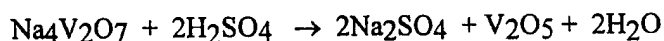
10   with the standard free energy at room temperature given by -326.4 kJ/mol.

Also, Na_2SO_4 is highly soluble in many polar liquids including of course water. Also, as long as $Na_4V_2O_7$ is present, $VOSO_4$ will not form.

In the preceding paragraphs, several reactions in water as a solvent are described. In some cases, the use of water as a solvent may lead to the formation of

15   hydroxides, e.g. $Al(OH)_3$. In such cases, instead of acids, the suitable reactants may be the respective gases; e.g. N_2O_5 instead of HNO_3 and SO_3 instead of H_2SO_4, and non-aqueous, polar solvents. The advantage of using non-aqueous solvents is that there is no possibility of the formation of $Al(OH)_3$, which must be heated to remove water thus risking agglomeration and coarsening. The possible use of other solvents

20   is discussed below. Table B gives a few of the possible reactions to form a number of oxide powders. All of the reactions are given with reactive gaseous species. Similar data can readily be given with aqueous acids as well.

Table B:

Some examples of the synthesis of fine ceramic powders by the present invention.

Ceramic Of Interest	Precursor	Chemical Reaction with Selective Solvent	Standard Free Energy, $\Delta G°$ (kJ/mol.)
Al_2O_3	$BaAl_2O_4$	$BaAl_2O_4 + CO_2 \rightarrow BaCO_3 + Al_2O_3$	- 113.19
Al_2O_3	$Ba_3Al_2O_6$	$Ba_3Al_2O_6 + 3CO_2 \rightarrow 3BaCO_3 + Al_2O_3$	- 459.51
Al_2O_3	$NaAlO_2$*	$2NaAlO_2 + SO_3 \rightarrow Na_2SO_4 + Al_2O_3$	- 342.6
Cr_2O_3	$MgCr_2O_4$	$MgCr_2O_4 + CO_2 \rightarrow MgCO_3 + Cr_2O_3$	- 6.93
Cr_2O_3	$MgCr_2O_4$	$MgCr_2O_4 + SO_3 \rightarrow MgSO_4 + Cr_2O_3$	- 188.13
ZrO_2	$BaZrO_3$	$BaZrO_3 + CO_2 \rightarrow BaCO_3 + ZrO_2$	- 88.33
ZrO_2	$BaZrO_3$	$BaZrO_3 + SO_3 \rightarrow BaSO_4 + ZrO_2$	- 336. 14
ZrO_2	$BaZrO_3$	$BaZrO_3 + N_2O_5 \rightarrow Ba(NO_3)_2 + ZrO_2$	- 260.3
TiO_2	$MgTiO_3$	$MgTiO_3 + 2HNO_3 \rightarrow Mg(NO_3)_2 + TiO_2 + H_2O$	- 81.07
TiO_2	Mg_2TiO_4	$Mg_2TiO_4 + 2CO_2 \rightarrow 2MgCO_3 + TiO_2$	- 77.34
TiO_2	Mg_2TiO_4	$Mg_2TiO_4 + 2SO_3 \rightarrow 2MgSO_4 + TiO_2$	- 440.82
TiO_2	Na_2TiO_3	$Na_2TiO_3 + CO_2 \rightarrow Na_2CO_3 + TiO_2$	- 80.62
TiO_2	Na_2TiO_3	$Na_2TiO_3 + SO_3 \rightarrow Na_2SO_4 + TiO_2$	- 325.81
V_2O_5	$Na_4V_2O_7$	$Na_4V_2O_7 + SO_3 \rightarrow 2Na_2SO_4 + V_2O_5$	- 458.01

*Standard free energy for $3Na_2SO_4 + Al_2O_3 \rightarrow 3Na_2O + Al_2(SO_4)_3$ at 298 K is +1,155 kJ/mol. showing that the formation of Na_2SO_4 is favored over that of $Al_2(SO_4)_3$. Thus, reaction of $NaAlO_2$ with SO_3 should proceed as shown. Also, while this reaction can be effected in water, a preferred is to identify a solvent with a high solubility for Na_2SO_4 but negligible for $NaAlO_2$. This is because of the possible formation of alumina precipitate which would tend to grow the particles. The formation of alumina using an aqueous solution of $NaAlO_2$ would be the conventional chemical precipitation process, and it is anticipated that in such a case a careful control of parameters would be necessary to prevent particle growth.

Table B shows that the standard free energies of the reactions are all negative suggesting that all of these reactions are thermodynamically favored. Carbonates, sulfates or nitrates of Al, Ti, and Zr are less stable than the corresponding alkaline earth compounds. No thermodynamic data appear to be available for the former.

Non-aqueous Solvents:

Reactions of the various oxides with CO_2, N_2O_5, and SO_3 to respectively form carbonates, nitrates, and sulfates can in principle be carried out in water or other polar

liquids. $Ba(NO_3)_2$ is soluble in water, but $BaCO_3$ and $BaSO_4$ are essentially

insoluble. There are a number of nonaqueous, polar liquids as possible candidates.

The prospective solvent to be used must have the following characteristics: (1) It must

have a reasonable solubility for the reacting gases, namely, CO_2, SO_3 or N_2O_5. (2) It

must have a significant solubility for $BaCO_3$, $BaSO_4$ or $Ba(NO_3)_2$. Table C gives a

list of possible candidates and their physical properties. It is important to note that the

boiling points of these liquids are quite high. Thus, as long as the solvent does not

chemically react with either the precursor or the product, the process can be carried

out over a wide temperature range. Also, the solubilities of $BaCO_3$, $BaSO_4$ and

$Ba(NO_3)_2$ should be greater at higher temperatures. At the same time, however, the

solubilities of the reacting gases in liquids decreases with an increasing temperature.

Thus, a suitable optimum temperature must be identified at which the reaction rate is

maximum.

Table C

Physical properties of some nonaqueous, polar liquids.

Material	Formula	b.p. (°C)	m.p. (°C)	Viscosity (millipois	Dielectric Constant	Density (g/ml)
Formamide	$HCONH_2$	210.7	2.55	39.7 at 20°C	111.5 at 20°C	1.135 at 18°C
N-Methyl -acetamide	$CH_3CONHCH_3$			24.13 at 50°C	151.8 at 50°C	0.9336 at 50°C
N-Methyl -formamide	$HCONHCH_3$	180	-5.4	19.9 at 15°C	200.1 at 15°C	1.007 at 15°C
N-Methyl -propionamide	$C_2H_5CONHCH_3$			60.6 at 20°C	185 at 20°C	0.9347
Propylene Carbonate		241	-49	25.3	64.4	1.19
Ethylene Carbonate	$(CH_2O)_2CO$	248	39	18.5	89.6 at 40°C	1.3218 at 39°C

The method of the present invention can also be used to synthesize doped

powders. For example, if the desired powder is Y_2O_3-doped ZrO_2 of composition

$Zr_{(1-x)}Y_xO_{(2-\delta)}$, then the starting precursor could be $BaZr_{(1-x)}Y_xO_{(3-\lambda)}$. After

reaction with HNO_3, as an example, the resulting powder should be $Zr_{(1-x)}Y_xO_{(2-\delta)}$.

Another example is RE-doped CeO_2, where RE is a rare earth, namely $Ce_{(1-}$

x)$RE_xO_{(2-\delta)}$, which can be made using doped $BaCeO_3$, that is, $BaCe_{(1-x)}RE_xO_{(3-\lambda)}$. In the preliminary work, nanosize Gd-doped CeO_2 was synthesized.

As already discussed, the method of the present invention can be used with water as the solvent in many cases. With water as the solvent, the corresponding aqueous acids, namely H_2CO_3 or H_2SO_4 or HNO_3, can be used, the choice of the acid being dependent upon the solubility of the leachable compound to be formed, assuming of course that the thermodynamics are favorable. For example, the synthesis of nanosize TiO_2 starting with $MgTiO_3$ using HNO_3 has been demonstrated. Further, if the leachable compound is Na_2SO_4 as in the formation of V_2O_5 starting with $Na_4V_2O_7$, H_2SO_4 should be the acid. However, with barium-containing compounds, HNO_3 is the acid of choice. There are two potential problems with water, however. (i) There is the potential for hydroxide formation . (ii) Agglomeration has been shown to occur readily when water is present. This may be avoided by replacing water with another solvent, and/or by supercritical drying. For the synthesis of RE-doped CeO_2 starting with $BaCe_{(1-x)}RE_xO_{(3-\lambda)}$ as a precursor, water is the ideal solvent since cerium hydroxide does not readily form. Preliminary work, discussed earlier, has indeed shown that nanosize ceria can be formed in an aqueous medium.

Example III

Synthesis of Nanosize Metallic Powders:

The present invention should also be useful for the synthesis of nanosize metallic powders, provided suitable intermetallic compounds can be used as precursors. There are numerous binary and ternary intermetallic compounds which may be used as precursors. As an example, for the synthesis of nanosize Pd, a possible precursor is BaPd which is an intermetallic line compound. The possible approach would consist of first fabricating BaPd by a conventional metallurgical process and then reacting it with an acid, e.g., HCl acid. It is readily shown that the $\Delta G°$ for the reaction,

$$BaCl_2 + Pd \rightarrow Ba + PdCl_2$$
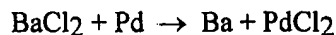
is positive suggesting that the first compound to form will be $BaCl_2$. The $BaCl_2$

formed will dissolve into water thus forming nanosize Pd powder. The so-formed Pd

powder should be nanosize and continue to remain nanosize since Pd has a negligible

solubility in water. Thus, as long as the concentration of HCl is low, and there is

BaPd to react with, that is, there is Ba to react with HCl; PdCl$_2$ will not form. Note

that this process differs from the synthesis of Pd by the reduction of PdCl$_2$. In the

latter case, particle growth of Pd readily occurs since the deposition of Pd on the

already formed Pd powder continues to occur as PdCl$_2$ in solution reacts with a

reducing agent, e.g., an alkali metal borohydride. In such a case, the experimental

conditions must be carefully controlled to prevent particle growth. By contrast, the

process of the present invention should readily lead to the formation of nanosize Pd

with negligible particle growth.

Advantages of the Method of the Present Invention over the other Synthesis Methods
for Nanosize Powders:

1)   Uniform mixing at a molecular or an atomic level

Since the powders are produced by leaching unwanted constituents from an

initial homogeneous solid solution or a compound, the remaining constituents should

be intimately mixed. For example, in the synthesis of Gd$_2$O$_3$-doped CeO$_2$ starting

with BaCe$_{(1-x)}$Gd$_x$O$_{(3-\delta)}$, Gd and Ce are expected to be intimately mixed since the

original solid solution is uniform.

2)   Narrow particle size distribution

Since the constituent to be removed, e.g., Ba is distributed on a regular,

periodic basis, it is anticipated that molecular level cracks or fissures are formed when

Ba is removed as Ba(OH)$_2$ or Ba(NO$_3$)$_2$. This should lead to a uniform particle size.

3)   Negligible growth of nanosize particles unlike in conventional chemical
synthesis:

The resulting nanosize particles in the present invention are essentially

insoluble in the liquid media used, and so are the precursors. As a result, growth is

not expected unlike conventional chemical synthesis approaches which rely on

- 22 -

precursors reacting in solution to form an insoluble product; e.g., the formation of insoluble Fe_3O_4 from Fe(II) and Fe(III) chlorides in solution. In such cases, growth of particles can readily occur.

While this invention has been described with reference to certain specific embodiments and examples, it will be recognized by those skilled in the art that many variations are possible without departing from the scope and spirit of this invention, and that the invention, as described by the claims, is intended to cover all changes and modifications of the invention which do not depart from the spirit of the invention.

CLAIMS

What is claimed is:

1.   A process for forming a nanosize ceramic powder comprising:

forming a precursor ceramic material comprising a fugitive constituent and a

non-soluble constituent in a single phase;

contacting the precursor material a selective solvent to form a solution of the

fugitive constituent and a residue of the non-soluble constituent,

the precursor sufficiently reactive with the solvent to form the solution of the fugitive

constituent in the solvent and form the nondissolved residue of the non-soluble

constituent

the precursor material and the non-soluble residue sufficiently insoluble in the solvent

such that there is insufficient precursor material and non-soluble residue in solution to

deposit and precipitate upon the residue of the non-soluble-constituent,

the fugitive constituent being sufficiently soluble in the solvent such that the precursor

reacts with the solvent to form a solution of the fugitive constituent without

precipitation and deposition of fugitive constituent upon the residue of the non-soluble

constituent in the form of nanosize particles;

removing the selective solvent solution from the residue to form a nanosize

powder of the non-soluble constituent.

2.   The process as in Claim 1 wherein the precursor is $BaCe_{(1-x)}RE_xO_{3-\delta}$ or

$SrCe_{1-x}RE_xO_{3-\delta}$ and the composition of the nanosize powder is $Ce_{1-x}RE_xO_{2-\delta}$ where RE

is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and about

0.13.

3.   The process as in Claim 1 wherein the precursor is $BaZr_{1-x}RE_xO_{3-\delta}$ or

$BaZr_{1-x}REXO_{3-\delta}$ and the composition of the nanosize powder is $Zr_{1-x}RE_xO_{2-\delta}$ where

RE is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and

about 0.13.

4.   The process as in Claim 1 wherein the composition of the resultant nanosize powder is Al_2O_3.

5.   The process as in Claim 3 wherein the precursor is selected from the group consisting of $BaAl_2O_4$, $Ba_3Al_2O_6$, and $NaALO_2$.

6.   The process as in Claim 1 wherein the composition of the resultant nanosize powder is Cr_2O_3.

7.   The process as in Claim 6 wherein the precursor is $MgCr_2O_4$.

8.   The process as in Claim 1 wherein the composition of the resultant nanosize powder is ZrO_2.

9.   The process as in Claim 8 wherein the precursor is $BaZrO_3$.

10.   The process as in Claim 1 wherein the composition of the resultant nanosize powder is TiO_2.

11.   The process as in Claim 10 wherein the precursor is $MgTiO_3$, or Mg_2TiO_4.

12.   The process as in Claim 1 wherein the composition of the non-soluble constituent and the nanosize powder is V_2O_5.

13.   The process as in Claim 12 wherein the precursor is $Na_4V_2O_7$

14.   The process as in Claim 1 wherein the selective solvent is water.

15.   The process as in Claim 1 wherein the selective solvent is an acid.

16.   The process as in Claim 15 wherein the acid is selected from the group consisting of HNO_3, HCl, H_2CO_3, and H_2SO_4.

17.   The process as in Claim 15 wherein the acid is contacted with the precursor with an acid gas.

18.   The process as in Claim 17 wherein the acid gas is SO_3, N_2O_5, CO_2 or HCl.

19.   The process as in Claim 1 wherein the selective solvent is a reacting gas dissolved in a non-aqueous polar solvent.

20.   The process as in Claim 19 wherein the polar solvent is selected from the group consisting of formamide, N-Methyl-acetamide, N-Methyl-formamide, N-Methyl-propionamide, propylene carbonate, and ethylene carbonate, and the reacting gas is selected from the group consisting of CO_2, SO_3, SO_2, and N_2O_5.

21.   A process for forming a nanosize metallic powder comprising:

forming a precursor metallic material comprising a fugitive metal constituent and a non-soluble metal constituent in a single phase;

contacting the precursor material a selective solvent to form a solution of the fugitive constituent and a non-dissolved residue of the non-soluble constituent, the precursor sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and form the non-dissolved residue of the non-soluble constituent

the precursor material and the non-soluble residue sufficiently insoluble in the solvent such that there is insufficient precursor material and non-soluble residue in solution to deposit and precipitate upon the residue of the non-soluble-constituent,

the fugitive constituent being sufficiently soluble in the solvent such that the precursor reacts with the solvent to form a solution of the fugitive constituent without precipitation and deposition of fugitive constituent upon the residue of the non-soluble constituent in the form of nanosize particles;

removing the selective solvent solution from the residue to form a nanosize powder of the non-soluble constituent.

22.   The process as in Claim 21 wherein the precursor is an alloy or an intermetallic compound.

23.   The process as in Claim 21 wherein the precursor is PaPd.

24.   The process as in Claim 21 wherein the selective solvent is an acid.

25.   The process as in Claim 21 wherein the selective solvent is HCl.

13

11

15

17
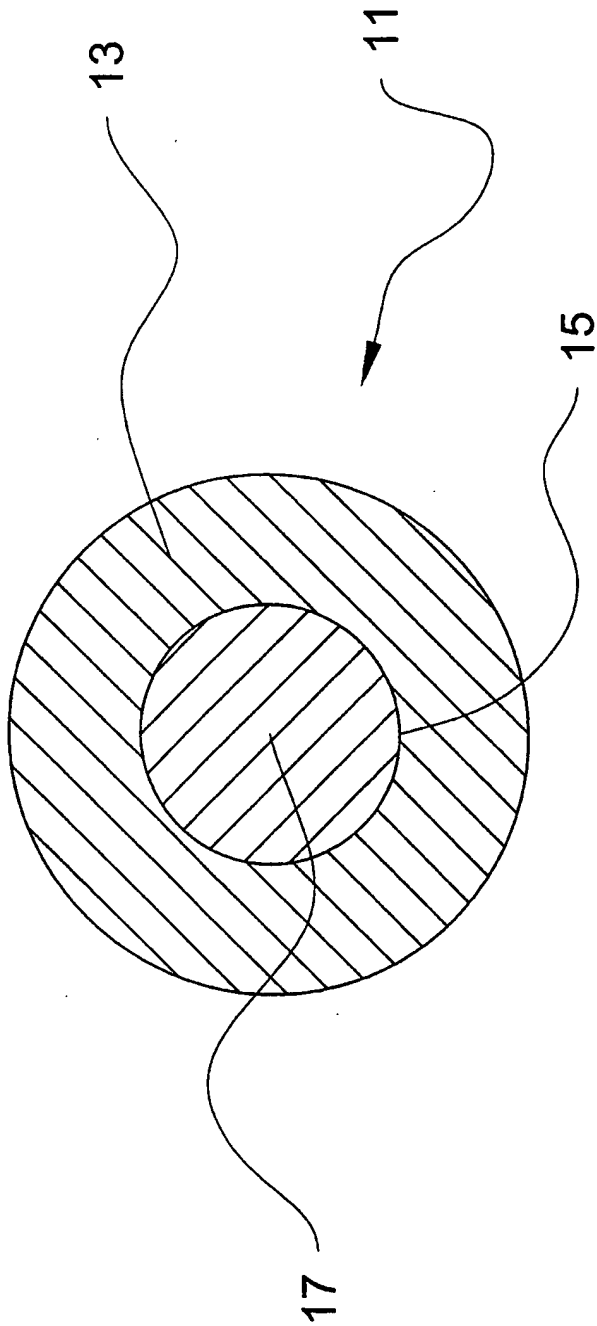
Fig. 1
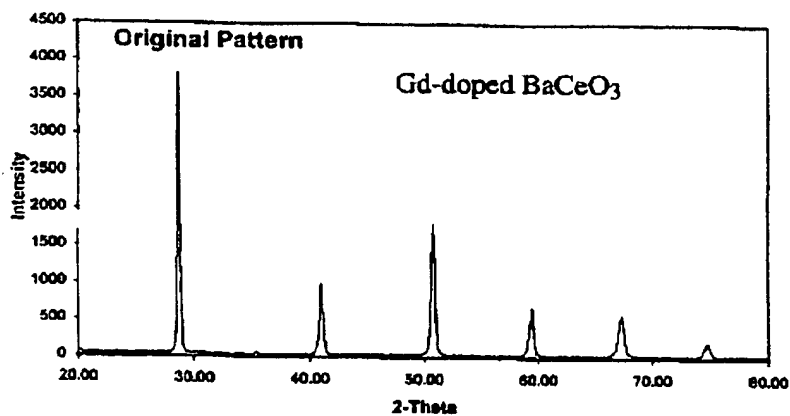
Fig. 2 (a)
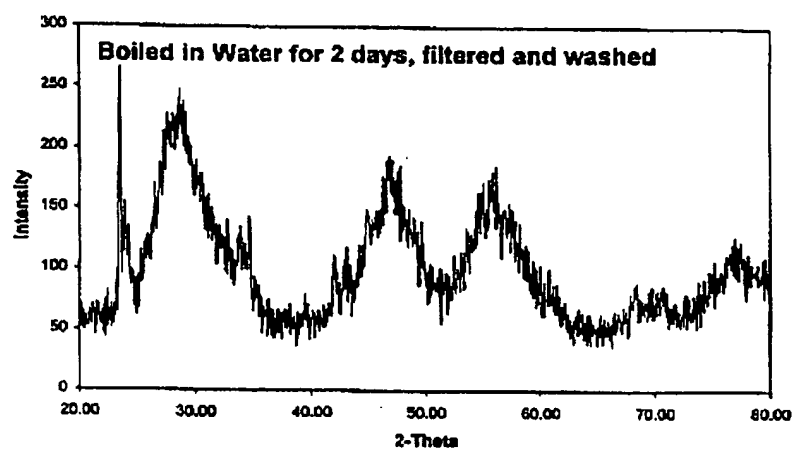
Fig. 2 (b)
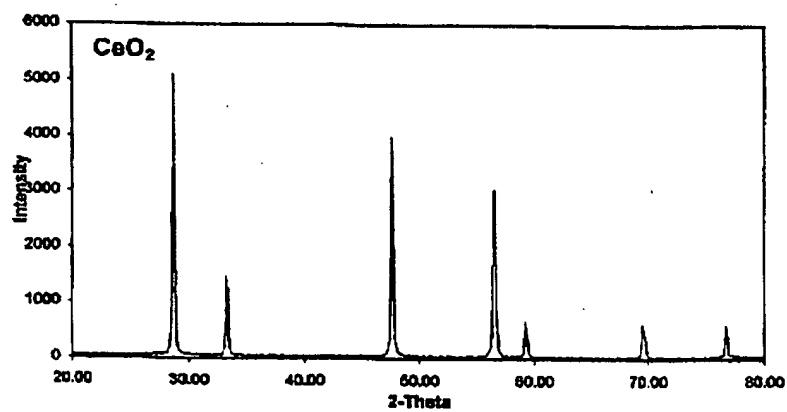
Fig. 2 (c)
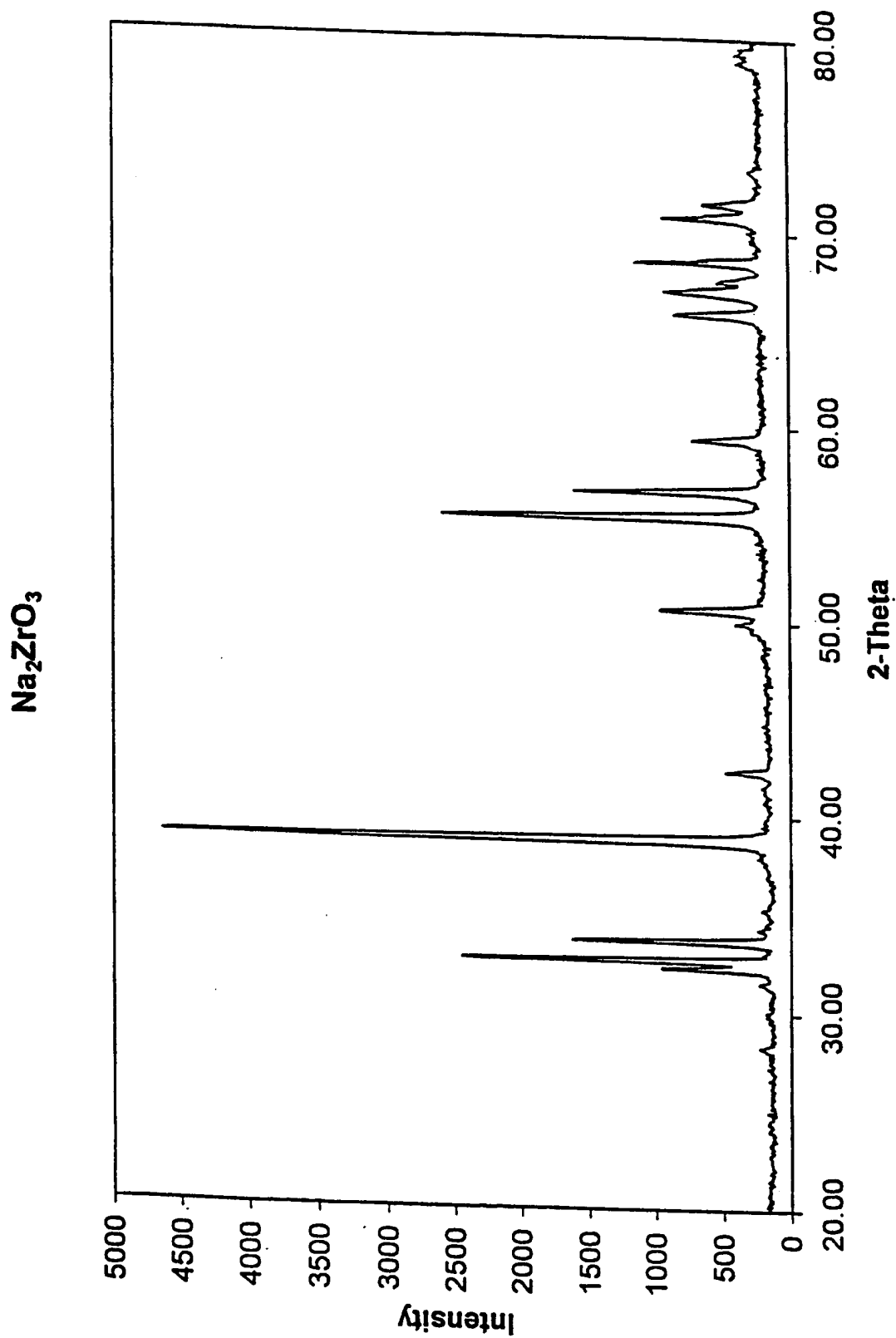
Figure 3(a)

Na2ZrO3 boiled in water for 10 min
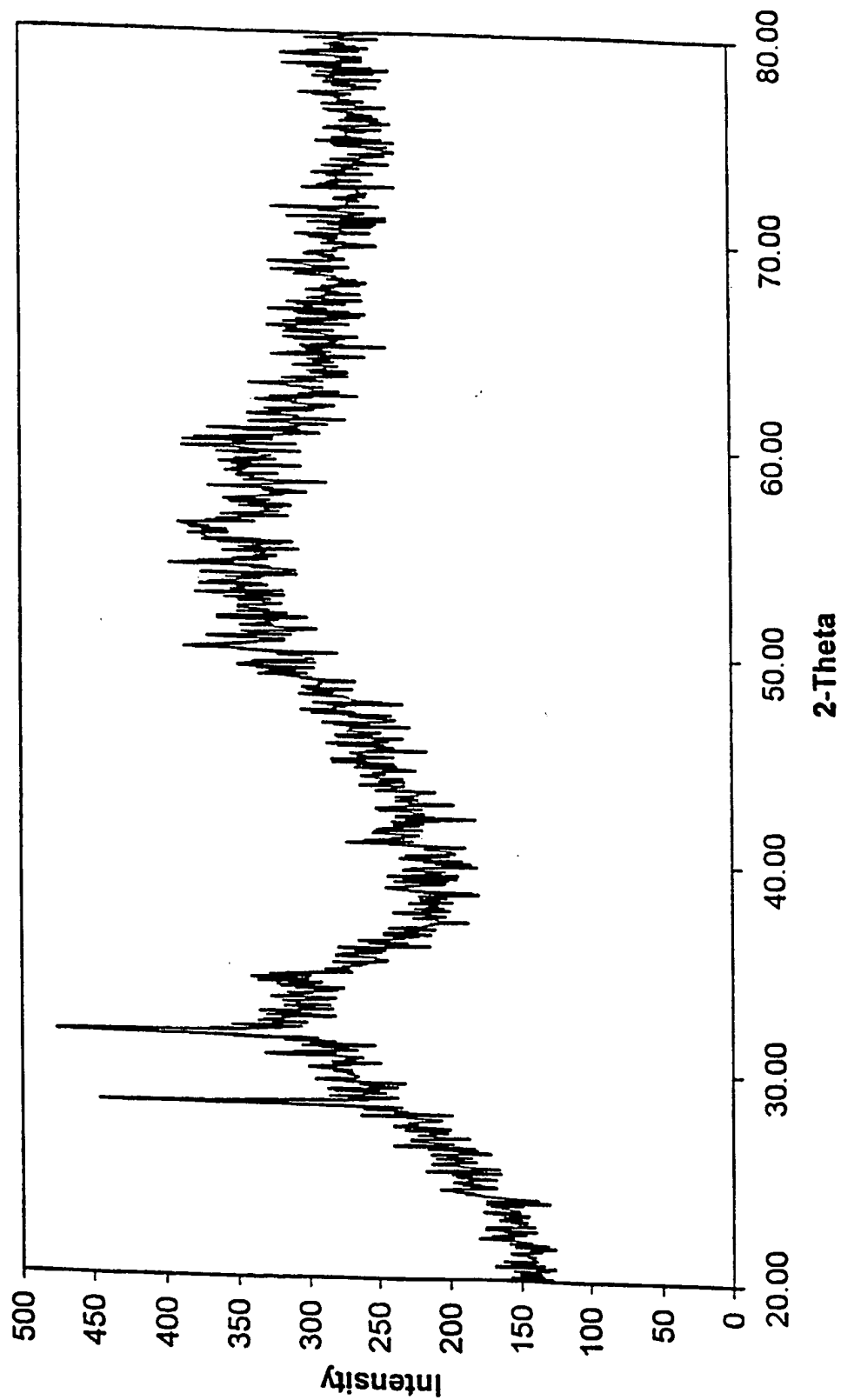
Figure 3(b)

Na2ZrO3 boiled in water for 10 min then at 100C, 1.5 hrs

2-Theta
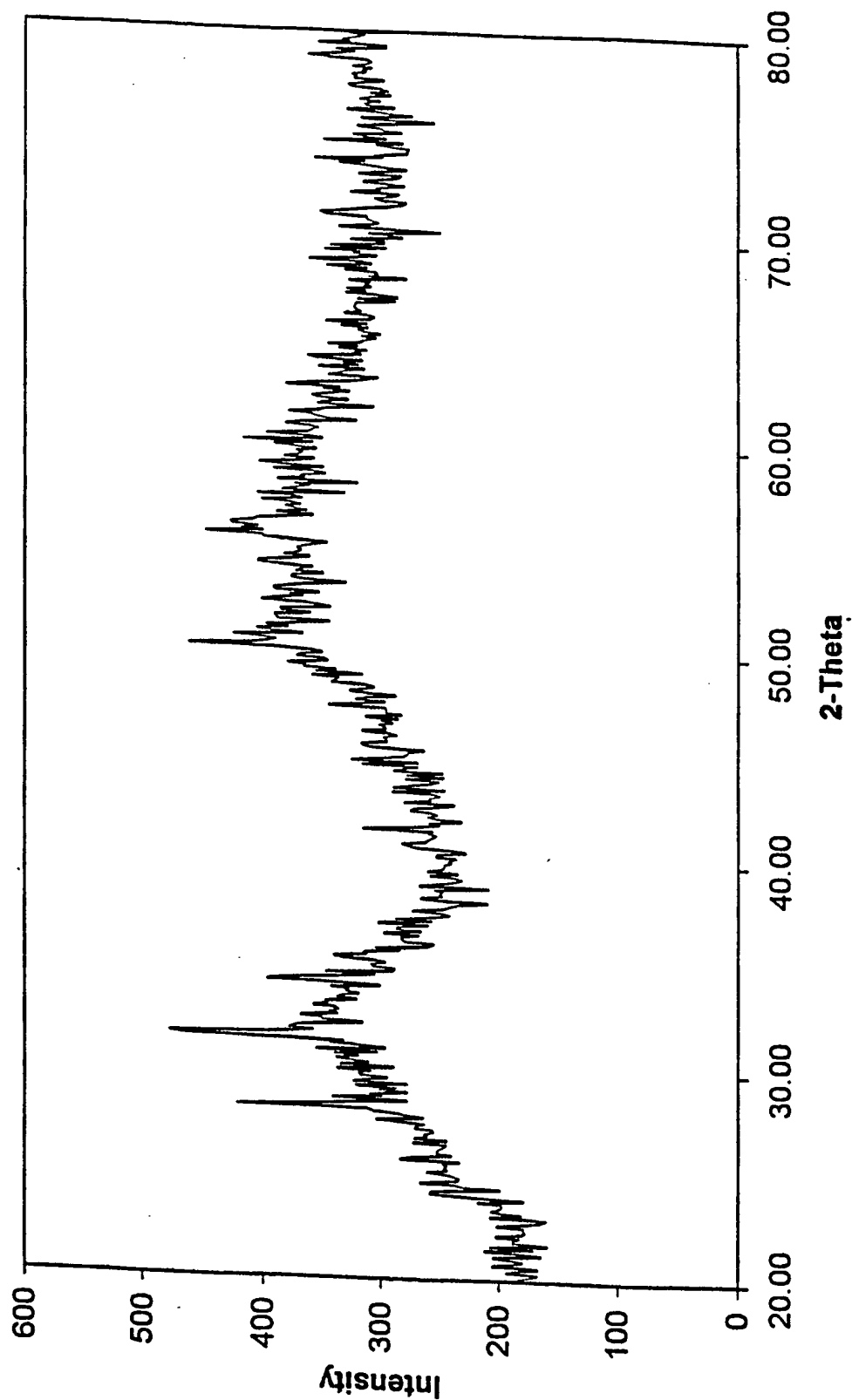
Figure 3(c)
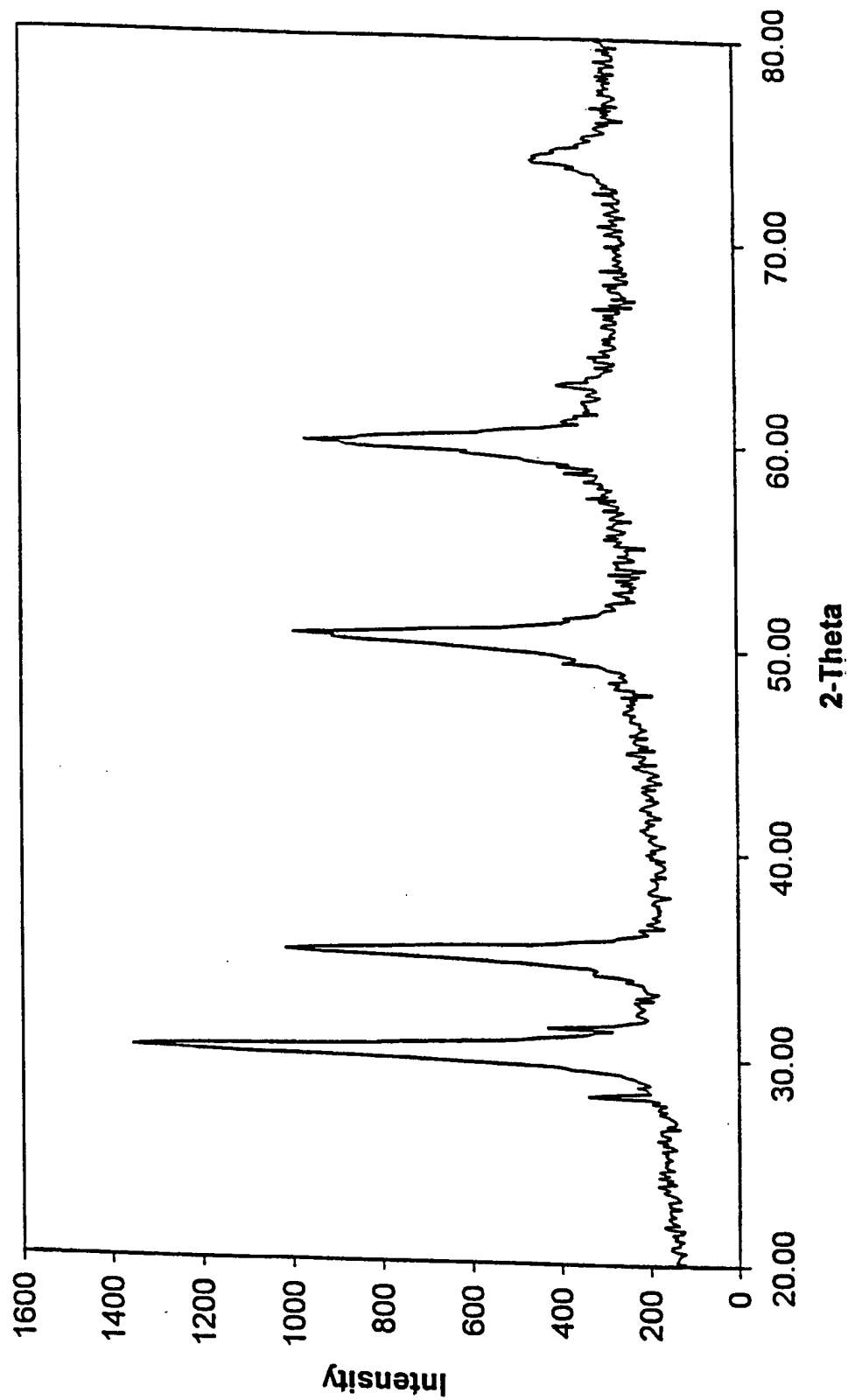
Na2ZrO3 boiled in water for 10 min then at 200C, 1.5 hrs
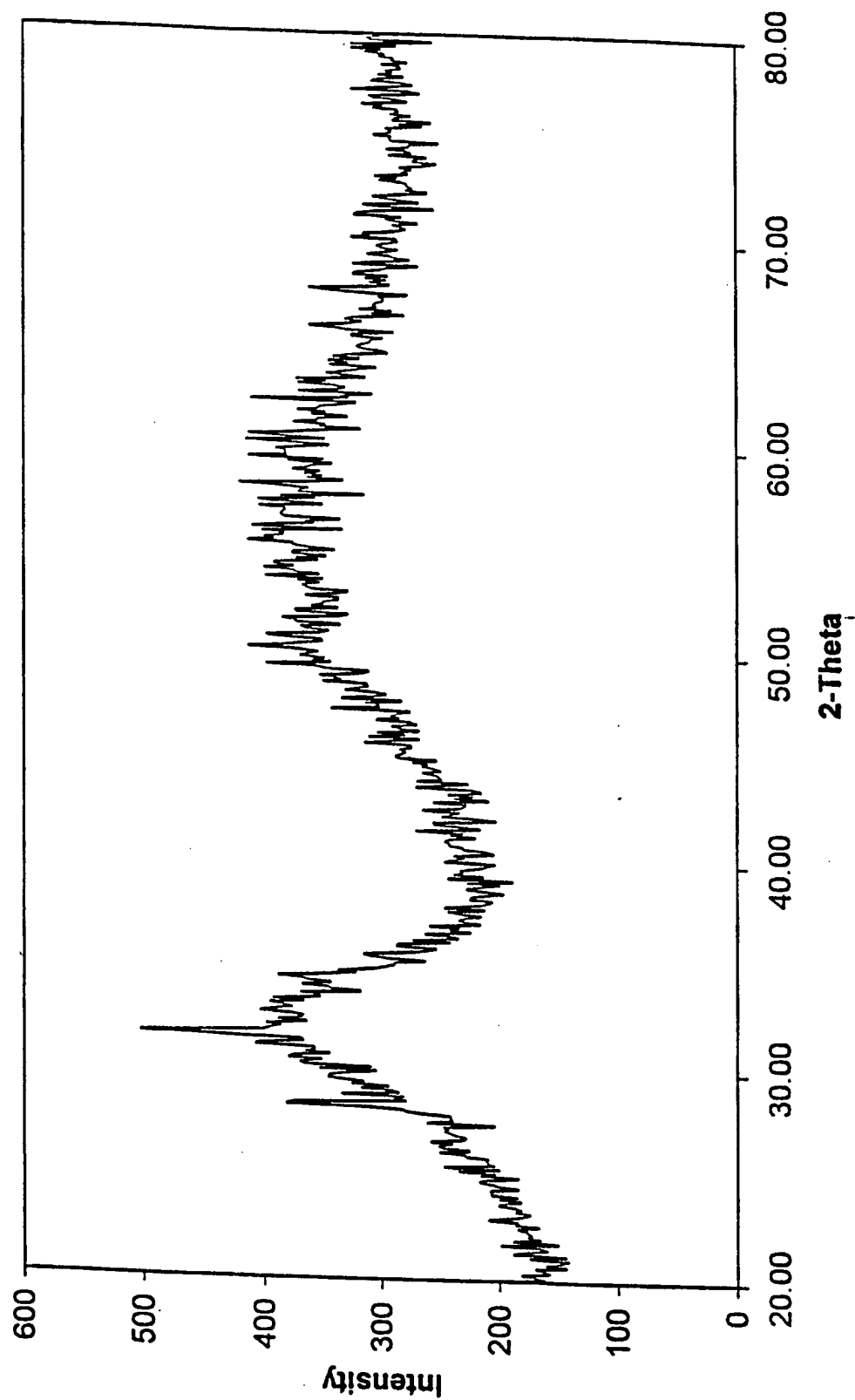
Figure 3(d)

Na2ZrO3 boiled in water for 10 min then at 300C, 1.5 hrs
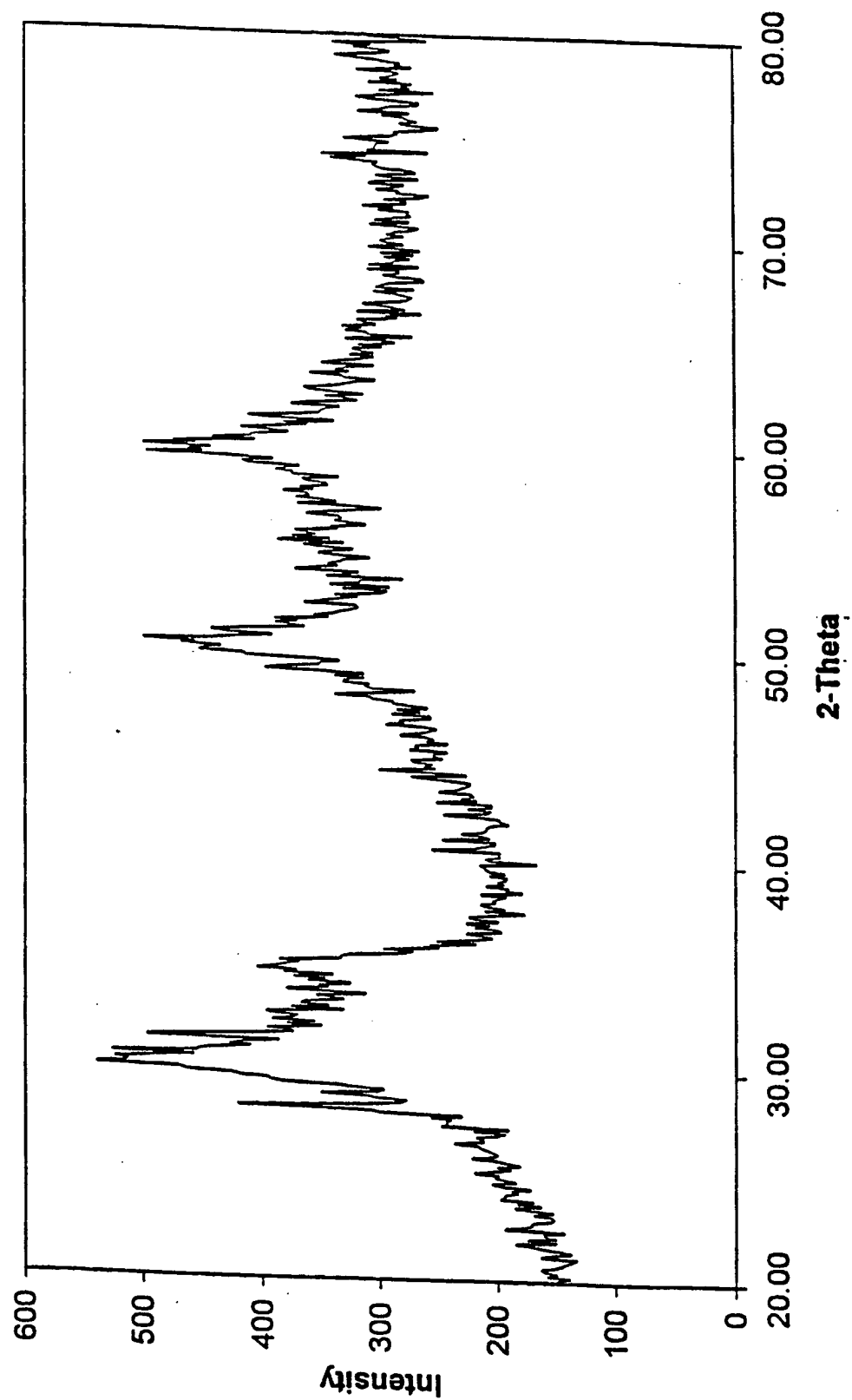
Figure 3(e)

Na2ZrO3 boiled in water for 10 min then at 350C, 1.5 hrs
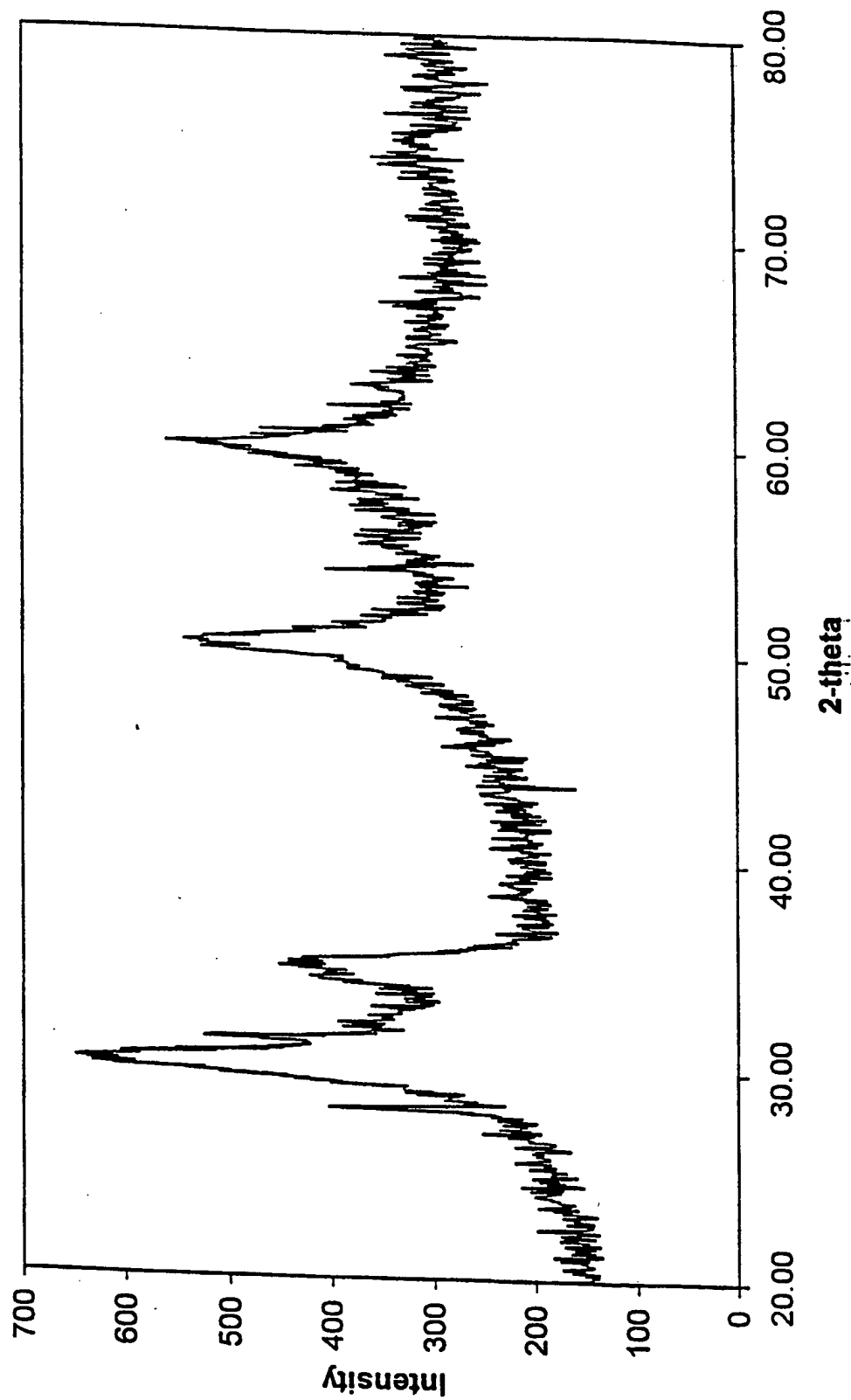
Figure 3(f)
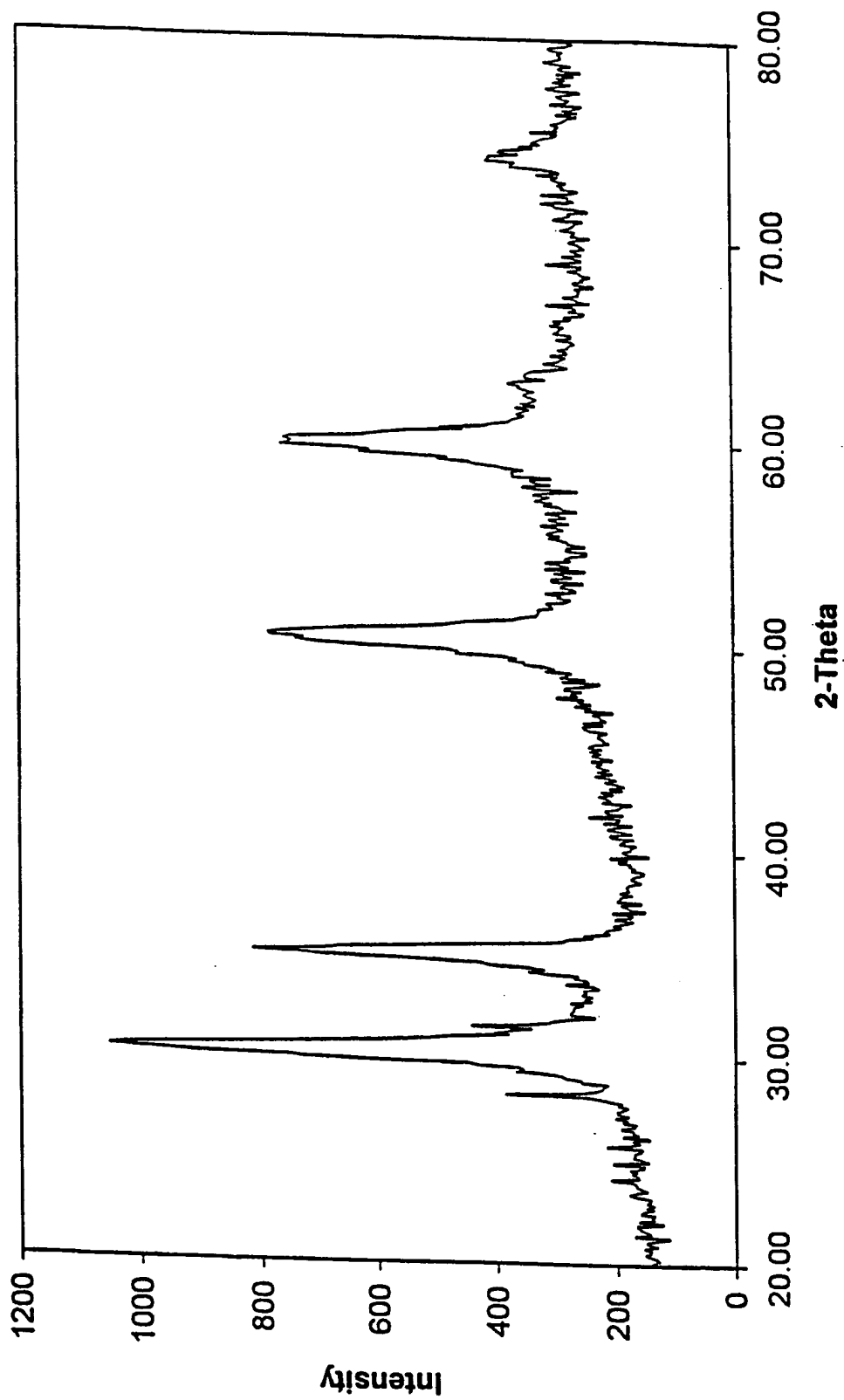
Figure 3(g)

Na2ZrO3 boiled in water for 10 min then at 500C, 1.5 hrs

Figure 3(h)

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO1F 17/00, 7/02; C01G 37/02, 25/02, 23/047; C22B 11/00
US CL :423/592, 263, 607, 608, 610, 625; 75/361, 370, 371, 373, 374

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/592, 263, 607, 608, 610, 625; 75/361, 370, 371, 373, 374

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST: nano$9, 423/263, 625, 607, 608, 610, 592, 75/$7.ccls.
EAST: 423/263, 625, 607, 608, 610, 592, 75/361, 370, 371, 373, 374

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,863,514 A (SASAKI et al) 26 January 1999, col. 2, lines 30-40.	1,10,14-16
X	WO96/34829 A (BURGARD et al) 07 November 1996, pp. 6,8.	1
X	US 5,759,230 A (CHOW et al) 02 June 1998, col. 2.	21
X,P	US 5,935,275 A (BURGARD et al) 10 August 1999, cols. 3-4.	1
A,P	US 5,961,938 A (YAMAMOTO) 05 October 1999, abstract.	1,21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 JANUARY 2000	1 0 FEB 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer STEVEN BOS Telephone No. 703-308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*